Drying of Ionic Liquid

by

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(ID: 11140)

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Chemical Engineering Programme

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in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

_____

(Dr. Lukman bin Ismail)

UNIVERSITI TEKNOLOGI PETRONAS
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MAY 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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MOHAMMAD NORAZRY BIN SULAIMAN

ABSTRACT

Room Temperature Ionic Liquids (RTILs) are salts in liquid phase. Continuous use of RTIL in a process may cause it to be contaminated with water and organic impurities over time. It is necessary to regenerate and purify the RTIL for recycle purposes. Drying is needed during pre-treatment and purification of IL solution before it can be used in any application to reduce weight, increase ease of handling and eliminate unwanted effects of moisture content towards IL properties. Drying process of ionic liquid is important since moisture levels that are too high may affect performance and reliability in most applications such as during synthesis of RTILs using aqueous solution to necessitate anion exchange and also in concentrating Benfield solution for recycles purposes during removal of CO_2. Therefore, to obtain the most optimum condition of drying for ionic liquids, the study on kinetic of drying is reported here by investigate the effects of different operating temperature towards drying of ionic liquid, effect of different anion and cation and drying using different equipment**.** Ionic liquids containing [bmim] cation with $[SO_4]$- or Phosphate-containing anion were used and drying methods applied were halogen lamp and vacuum drying methods. Thermogravimetric analysis which measures change of mass over time throughout the drying process was used to generate primary drying curves which were then manipulated to get secondary kinetic data. The drying process mainly occurred during falling rate period. Samples dried under higher temperature using vacuum drying have higher maximum drying rates, lower final moisture contents, higher drying constants and shorter drying times. The same result is observed for samples containing smaller anion.

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TABLE OF CONTENTS

CERTIFICATION OF APPROVAL i

CERTIFICATION OF ORIGINALITY ii

ABSTRACT iii

ACKNOWLEDGEMENTS iv

TABLE OF CONTENTS v

LIST OF FIGURES vii

LIST OF TABLES viii

ABBREVIATIONS AND NOMENCLATURES ix

CHAPTER 1 INTRODUCTION 1

1.1 Background Study 1

1.2 Problem Statement 4

1.3 Objectives 5

1.4 Scope of Study 5

CHAPTER 2 LITERATURE REVIEW AND THEORY 6

2.1 Chronological Development of Ionic Liquid Study 6

2.2 The Drying Curve 7

2.3 Kinetic of Drying 9

CHAPTER 3 METHODOLOGY/PROJECT WORK 13

3.1 Sample Preparation 13

	3.2 Research Methodology and Experimental Procedure/Approach	16
	3.3 Chemical, Equipment, and Apparatus Required	20
	3.4 Key Milestones	21
	3.5 Gantt Chart	22
CHAPTER 4	RESULTS AND DISCUSSION	23
	4.1 Overview	23
	4.2 Effect of Drying Temperature	24
	4.3 Effect of Different Types of Cation and Anion	26
	4.4 Effect of Different Drying Methods	33
CHAPTER 5	CONCLUSION AND RECOMMENDATION	35
REFERENCES		37
APPENDIX		39

LIST OF FIGURES

Figure 1.1	Common Cation in Ionic Liquids	2
Figure 1.2	Characteristics of Batch Dryer	3
Figure 1.3	Characteristics of Continuous Dryer	4
Figure 2.1	Expected Plots of Total Moisture Content and Drying Rate Versus Time	7
Figure 2.2	Expected Drying Curve from Moisture Analyzer	8
Figure 2.3	Kinetic of Drying	11
Figure 2.4	Drying Rate and Temperature Curves for Particle	12
Figure 3.1	Initial Moisture Content Test using Karl Fisher Titration Equipment	13
Figure 3.2	Sample are Weighed using Mass Balance	14
Figure 3.3	Sample Preparation	15
Figure 3.4	Sample Setup in Thermal Scientific Vacuum Drying Oven	17
Figure 3.5	Mettler TOLEDO Halogen Moisture Analyzer	19
Figure 4.1	Drying Curve of Moisture Content versus Time at Different Temperature	25
Figure 4.2	Drying Curve of Drying Rate versus Time at Different Temperature	25
Figure 4.3	Drying Curve of Moisture Content versus Time for [bmim] cation	29

Figure 4.4	Drying Curve of Drying Rate versus Time for [bmim] cation	29
Figure 4.5	Drying Curve of Moisture Content versus Time for [SO4] Anion	30
Figure 4.6	Drying Curve of Drying Rate versus Time for [SO4] Anion	31
Figure 4.7	Drying Curve of Moisture Content versus Time for Phosphate Anion	32
Figure 4.8	Drying Curve of Drying Rate versus Time for Phosphate Anion	32
Figure 4.9	Comparison of Drying Curves for Moisture Content versus Time	34
Figure 4.10	Comparison of Drying Curves for Drying Rate versus Time	34

LIST OF TABLES

Table 2.1	Chronological Development in Study of Ionic Liquid	6
Table 3.1	Sample Preparation	14
Table 3.2	Equipment, Apparatus, and Chemical Used	20
Table 4.1	Molecular Structures of Ionic Liquid	27

ABBREVIATIONS

RTILs	Room-Temperature Ionic Liquids
GPU	Gas Permeation Unit
NA	Not Applicable
MR	Moisture Ratio
ppm	parts per million
[bmim][MeSO4]	1-butyl-3-methylimidazolium methylsulfate
[emim][HSO4]	1-ethyl-3-methylimidazolium hydrogensulfate
[bmim][(C2F5)3PF3]	1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate
[mmim][DMP]	1,3-dimethylimidazolium dimethylphosphate
[bmim][Cl]	1-butyl-3-methylimidazolium chloride
[bmim][DCA]	1-butyl-3-methylimidazolium dicyanamide

NOMENCLATURE

Symbol	Definition	[SI unit]
K	Drying Rate Constant	[min-1]
Ea	Activation Energy	[J/mol]
T	Temperature	[C]
t	Time	[min]
R	Gas Constant	[J/mol]
MC	infinity Final Moisture Content	[%]

CHAPTER 1

INTRODUCTION

1.1 Background Study

Ionic liquids are low melting point salts that represent an exciting new class of reaction solvents for catalysis (Gordon, 2001). The history of ionic liquids goes back to 1914 by Walden with the founding of the synthesis of ethylammonium nitrate. This material is formed simply by the reaction of ethylamine with concentrated nitric acid, but its discovery did not prompt any great amount of interest at the time. Most of the salts employed still displayed melting points above room temperature. Only in 1948, Hurley and Weir developed room temperature liquid chloroaluminate melts for applications in aluminium electroplating.

Ionic liquids are usually composed of large asymmetric organic cations and inorganic or organic anions. They exhibit unique properties compared to other solvents. Ionic liquids are generally colorless liquids with relatively high viscosities where they exhibit very low vapor pressures under ambient conditions and thus are effectively non-volatile. Ionic liquids are good solvents for a broad spectrum of inorganic, organic and polymeric materials and are immiscible with numerous organic solvents. Some properties, such as the thermal stability and miscibility, mainly depend on the anion, while others, such as the viscosity, surface tension and density, depend on the length of the alkyl chain in the cation. The most commonly employed ionic liquid anions are polyatomic inorganic species meanwhile the most prominent cations are pyridinium and an imidazolium ring species with one or more alkyl groups attached to the nitrogen or carbon atoms. At the same time, the presence of the alkyl chain on the cation determines the solubility of the Ionic liquids in less polar fluids. The properties of the ionic liquids can significantly change by varying the length of the alkyl groups that are incorporated into the cation and the types of anions. The cations of ionic liquids are often large organic cations, like imidazolium, pyridinium, pyrrolidinium, quaternary ammonium or phosphonium ions.

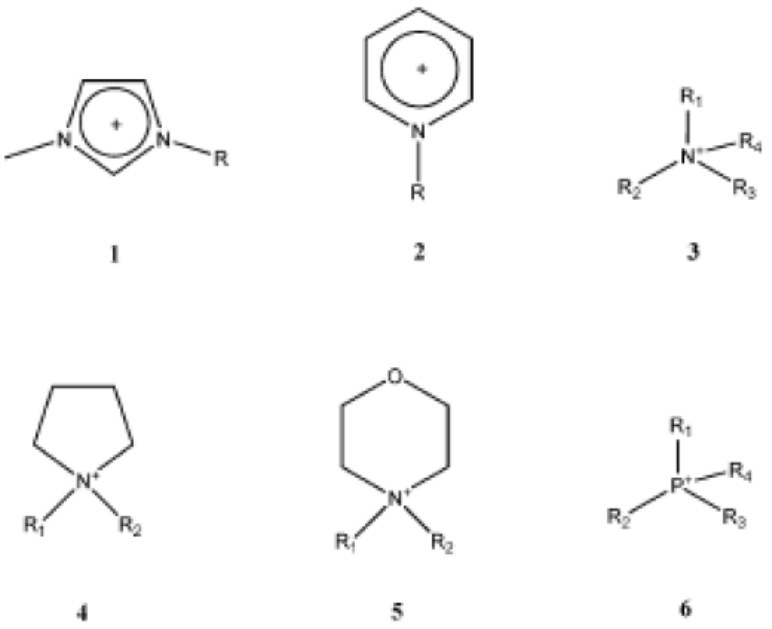


FIGURE 1.1 Common Cations in Ionic Liquids: (1) 1-alkyl-3-methylimidazolium; (2) 1- alkylpyridinium; (3) quaternary ammonium; (4) 1,1-dialkylpyrrolidinium; (5) 1,1- dialkylmorpholinium; (6) phosphonium (Binnemans, 2006)

The 1-alkyl-3-methylimidazolium ions are often used as the cationic part of ionic liquids. Cl- and Br- yield hydrophilic ionic liquids which are miscible with water and fluorinated anions like [PF6]- allow preparation of hydrophobic ionic liquids that are immiscible with water. Hydrophobicity of ionic liquids containing [BF4]- depends on the alkyl chain length of the associated cation whereby increasing alkyl chain length from butyl to hexyl to octyl increases hydrophobicity. Due to their hydrophobicity, they can be dried to very low final water contents.

Ionic liquids have been applied in different areas of separation, such as ionic liquid supported membranes, as mobile phase additives and surface-bonded stationary phases in chromatography separations and as the extraction solvent in sample preparations, because they can be composed from various cations and anions that change the properties and phase behavior of liquids. Although the applications of ionic liquids in separation are still in their early stages, the academic interest is increasing. An overview of the principle applications of ionic liquids in separation technology is present in this work. Furthermore, the prospects in separation techniques are discussed.

Drying can be defined as a unit operation in which a liquid-solid separation is accomplished by the supply of heat, with separation resulting from evaporation of liquid (Van't Land, 2012). The screening procedures that offer a preliminary choice for a specific drying duty are described in order to get the most appropriate drying process. Since there are two typical categories of drying technologies which are batch dryer and continuous dryer, thus the criteria for judging on both types are basically do not vary from one to another. The preliminary parameters to be examined are moisture content, particle-size distribution, bulk density, hardness of the particle, dusk content, flow characteristics, dispersibility, caking tendency, and dissolution tendency.

FIGURE 1.2 Characteristic of Batch Dryer

Figure 1.2 shows the characteristics of sample to be processed using batch dryer where by combining certain number of characteristics would lead to one specific dryer. According to Van't Land, 2012), should the sample have maximum product temperature of less than 30°C, with no oxidation occurrence and zero toxicity, so the dryer to be used is fluidized-bed drying or fluid-bed granulation. The sample has minute flammable vapor and does not require agitation process, thus the suitable dryer would be tray dryer or agitated pan dryer.

Same goes with the selection of continuous dryer. From figure 1.3 below, according to Van't Land (2012), for instant, if the sample has small particle size plus maximum product temperature of 75°C, the appropriate equipment might be a spray dryer.

FIGURE 1.3 Characteristics of Continuous Dryer

1.2 Problem Statement

Ionic liquids have been used mainly as solvents in many aspects. The interaction of ionic liquids with other particles would lead to the formation of aqueous ionic liquid solutions and this has been the subject of recent studies. Water molecules can form hydrogen bonds with ionic liquid cations and anions. At low water concentration, water molecules will tend to react with anions rather than with other water molecules and form clusters at high water concentration. Furthermore, the properties of ionic liquids can be highly dependent on water concentration, especially at low concentration. Thus, from the effects of water content in ionic liquid, drying or water removal is necessary to produce dry ionic liquid.

The significant of producing dry ionic liquid is as an alternative to dry water or dry gel because they tend to collapse due to the temporal water vaporization in an open system. Dry ionic liquid is free from this undesirable defect due to its non-volatility. Therefore, this work will contribute in the subject of drying kinetic for ionic liquid in order to analyze the optimum drying condition for ionic liquids based on drying curves analysis liquids based on drying curves analysis.

1.3 Objectives

The aim of this project is to study the kinetic of drying process for ionic liquids under different operating parameters and conditions.

The objectives are:

1. To investigate the effects of different operating temperature towards drying of ionic liquid.
2. To investigate the effect of different anion and cation
3. To investigate the drying process of ionic liquid via different drying methods

1.4 Scope of Study

In conjunction with the objectives, the scope of studies will cover three variable parameters. First part will be focusing more on the effect of different operating temperature onto the drying behavior of ionic liquid thus two main parameters will be monitored which are temperature profile and drying behavior of ionic liquids.

Furthermore, to investigate the performance of different drying methods in drying ionic liquids, two different processes will be used in this study. The first method will be vacuum drying whereby the ionic liquid sample is dried by means of hot circulating air under vacuum condition. The second method is by using halogen lamp drying whereby the heating element comprises of a glass tube filled with inert halogen gas containing a tungsten wire heating element.

Apart from different drying methods, different combination of ionic liquid anion and cation consisting of [bmim] cation, [SO4]- and Phosphate-containing anion are also chosen since their molecular structures and diameters are different from each other and these may also affect the drying process and kinetic of the ionic liquid samples.

CHAPTER 2

LITERATURE REVIEW AND THEORY

This chapter focus on the analytical, critical and objective review of written materials on kinetic study of drying for ionic liquids. It was found out that drying of ionic liquids have been done by many researchers for the purpose of purification of ionic liquid for their experiments. However, there is not much emphasis on the behavior of ionic liquid during the drying process itself especially on the kinetic part.

2.1 Chronological Development of Ionic Liquid Study

TABLE 2.1 Chronological Developments in Study of Ionic Liquid

No.	Development in Ionic Liquid	Year	Contributors
1.	Discovery of the first ionic liquid, ethanolammonium nitrate.	1888	Gabriel and Weiner
2.	Synthesis of earliest RTILs, ethylammonium nitrate.	1914	Paul Walden
3.	First ionic liquid patent was introduced which claimed that certain organic salts are able to dissolve cellulose.	1934	NA
4.	Ionic liquids based on alkyl-substituted imidazolium and pyridinium cations with halide or tetrahalogenoaluminate anions were developed for use as electrolytes in batteries.	1970 to 1980	NA
5.	Imidazolium is recognized as the most stable ionic liquid cation.	1982	Wilkes and Hussey
6.	A study on solution thermodynamics of imidazolium-based ionic liquids in water was conducted.	2001	Anthony, Maginn and Brennecke
7.	Relationship between water content and physical properties of aliphatic quaternary ammonium imide-type ionic liquid containing metal ions was established.	2005	Katase, Imashuku, Murase,Hirato and Awakura
8.	Interaction of ionic liquid with water with variation of water content in 1-butyl-3-methyl-imidazolium hexafluorophosphate was investigated.	2007	Seth, Chakraborty, Setua, and Sarkar
9.	Development of membrane drying of ionic liquid solutions by using reverse osmosis technique.	2011	Lipscomb and Du

2.2 The Drying Curve

Once all the experiments are done, there will be theoretically expected result to be estimated the accuracy and precision. In order to analysis upon the kinetic of drying, moisture content measurement is done individually for effect of cation and anion of ionic liquid, different solvent, drying of ionic liquid on solid supports, static versus dynamic condition (air flow) and dying curve under non isothermal condition (variable temperatures). By using modern portable moisture balances with built in infrared heaters, the experiment could be done to measure the moisture content of the product and gives a profile of moisture content variations with time. The curve of moisture content as a function of time is then plotted. While different samples and different conditions of drying often give rise to curves of very different shapes in the falling rate period, the curve in Figure 2.1 occurs frequently and is expected for most of the experimental setups in this study.

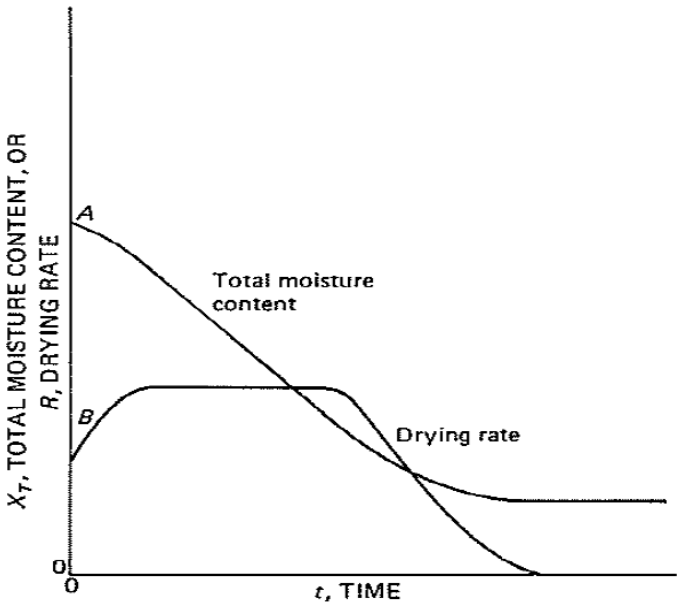


FIGURE 2.1 Expected Plots of Total Moisture Content and Drying Rate versus Time (McCabe et al., 1993)

Another factor that is expected at the end of the project is the drying rate versus total moisture content. Figure 2.2 represents a plot of total moisture content and drying rate versus time whereby drying occurs in three different periods (McCabe et al., 1993). The first stage is where sensible heat is transferred to the product and the contained moisture. This is the heating up of the product from the inlet condition to

the desired condition. During this period, the rate of evaporation increases dramatically with mostly free moisture being removed.

Moving on to the second phase of constant rate period, free moisture persists on the surfaces and the rate of evaporation alters very little as the moisture content decreases. During this period, drying rates are high and higher inlet air temperatures than in subsequent drying stages can be used without detrimental effect to the product. There is a gradual and relatively small change in the product temperature during this period. The next stage will be falling rate period during which migration of moisture from the inner interstices of each particle to the outer surface becomes the limiting factor that reduces the drying rate.

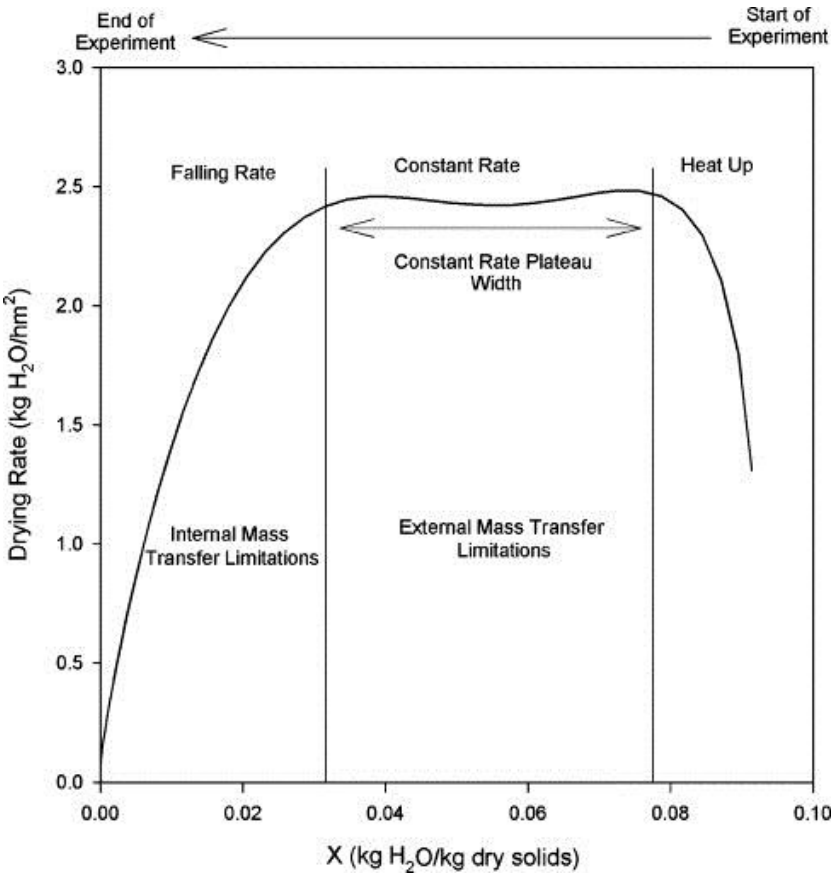


FIGURE 2.2 Expected Drying Curve from Moisture Analyzer

2.3 Kinetic of Drying

A series of work and studies on the kinetic of drying by thermal analysis have been performed previously by researchers to determine the kinetic data from the whole drying process of any materials. According to Pope et al. (1977), to extract the data for kinetic information, we have to recognize a reaction mechanism from the shape of the weight loss curve. Where a single mechanism predominates, as in the case of gas phase or solution reactions, it is often possible to describe the reaction by a general rate law:

$$\frac{dC}{dt} = k(1 - C)^n$$

where: C = fractional conversion

t = time (min)

k = rate constant (min-1)

n = reaction order

Consider the reaction:

$$A \rightarrow \text{ Products}$$

If first order kinetic is followed, then the rate of the reaction is proportional to the concentration of A:

$$\text{Rate} = k \text{ (concentration A)}$$

In the case of drying the reaction is:

$$(H_2O) \text{ absorbed} \rightarrow (H_2O) \text{ Gas}$$

Let α be the concentration of (H_2O) absorbed at t=0 and (α-x) be the concentration of (H_2O) absorbed at any other time denoted by t. The reaction rate for desorption is $\frac{dx}{dt} = k(\alpha - x)$. On integration, this equation becomes:

$$k = \frac{1}{t}\ln(\frac{\alpha}{\alpha - x})$$

The k values calculated can be used to plot a kinetic graph of ln k against 1/T (Figure 2.2) which will produce a reasonable straight line with gradient –E/R whereby R is the gas constant according to:

$$\ln k = \ln Z - \frac{E}{RT}$$ (Z is Arrhenius frequency factor, min^{-1})

Thus, the activation energy, E (J/mol), can be directly obtained from the plot. Furthermore, all the kinetic value can also be used to approximate the theoretical drying time at any temperature via the following equation:

$$t\ (drying\ time) = \frac{4.5 \times 0.0113}{k_T}$$

where: t = drying time at the desired temperature (min)

k_T = calculated rate constant at the desired temperature, T (min^{-1})

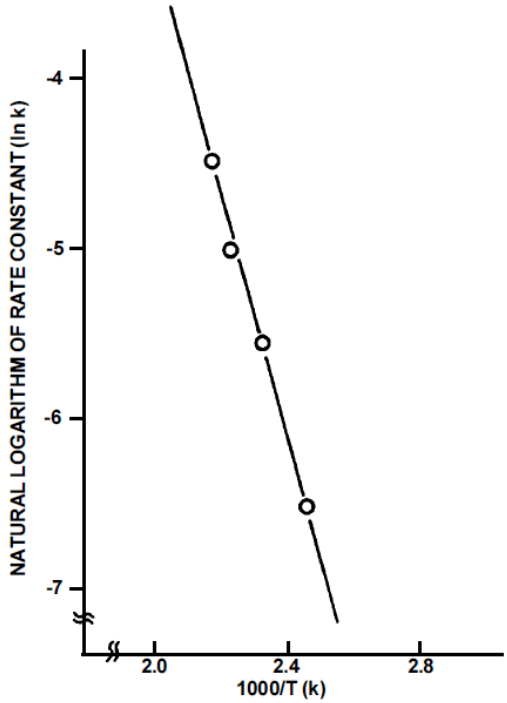


FIGURE 2.3 Kinetic of Drying (Pope et al., 1977)

Furthermore, an analysis done by Kemp et al. in 2001 suggested several methods for processing the kinetic data obtained from drying. Generally, the approach in analyzing the kinetic data will depend on several factors; particle size, initial and final moisture content, predominant drying regime (unhindered or falling-rate), air velocity, level of accuracy required for the data and availability of measuring equipment. All these data will be used to generate useful drying curves that are interrelated such as Figure 2.4 (a) showing drying curve obtained directly from weight loss-time data (moisture content vs. time). In addition, Figure 2.4 (b) plots drying rate curve obtained directly from humidity-time data (drying rate vs. time) while Figure 2.4 (c) represents time independent or Krischer curve derived from the combination of the previous curves (drying rate vs. moisture content). It is used as the basis for the characteristic curve scaling method. Finally, Figure 2.4 (d) shows a temperature-time plot representing how the sample temperature varies during the experiment.

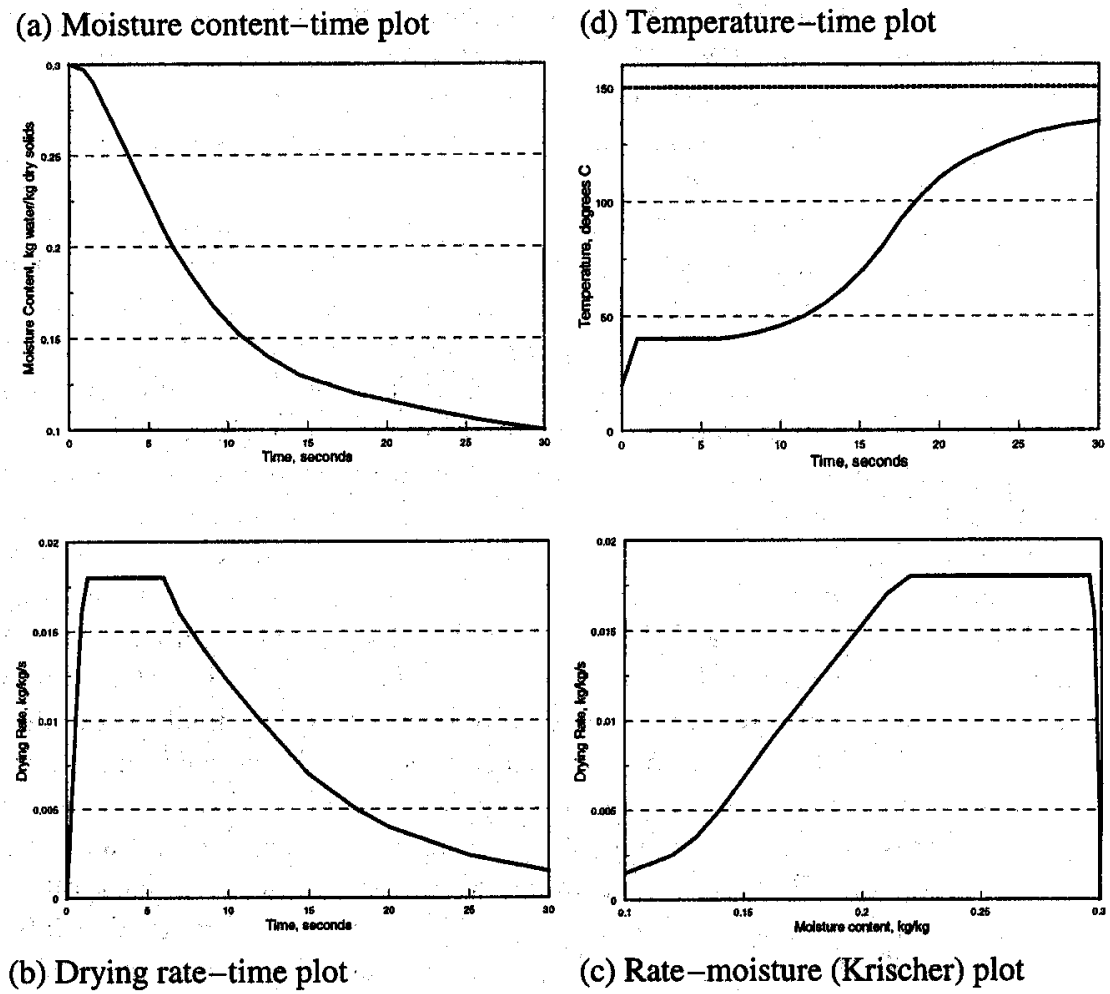


FIGURE 2.4 Drying rate and temperature curves for a particle (Kemp et al., 2001)

Figure 2.4 shows the four interrelated curves obtained by simulation of a single particle undergoing convective drying in a hot air stream at a constant 150°C. This approach can be applied to the drying of ionic liquids since under the chosen conditions, the material is assumed to show an induction (initial heating) stage, unhindered drying (constant rate) period and a hindered drying (falling rate) period.

CHAPTER 3

METHODOLOGIES / PROJECT WORK

3.1 Sample Preparation

Initially, raw ionic liquid will be prepared with the amount of 3.5g for each sample (there will be six types of ionic liquid to be used throughout the whole experiment processes) and extra 15g for ionic liquid sample number 3. Initial moisture content of raw ionic liquids will be measured using Karl Fisher Titration.

The test can be done in two term, liquid form and solid form. Most of the raw ionic liquids to be used in the experiment are in liquid phase except sample (3). For liquid sample, the ionic liquids need to be injected directly into the solvent (the left circle in the picture) using needle and syringe while the solid sample will be put into specific vial (in the right circle) to be analyzed. The test would take around 1 to 5 minutes to be completed depend on the amount of the sample and the composition of the solvent.

FIGURE 3.1 Initial Moisture Content Test using Karl Fisher Titration Equipment

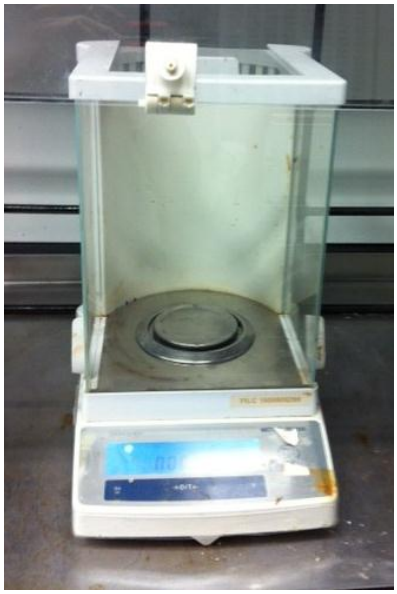


FIGURE 3.2 Samples are weighed using Mass Balance

Later each sample will be mixed with same amount of distilled water to jive with water ratio of 1:1. Details data for the sample preparation is shown in Table 3.1 below.

TABLE 3.1 Sample Preparations

Sample Preparation				
Indicator	**Nomenclature**	**Ionic Liquid**	**Initial weight (g)**	**Initial Distilled Water (g)**
1	[bmim][MeSO4]	1-butyl-3-methylimidazolium methylsulfate	3.5	3.5
2	[emim][HSO4]	1-ethyl-3-methylimidazolium hydrogensulfate	3.5	3.5
3	[mmim][DMP]	1,3-dimethylimidazolium dimethylphosphate	3.5	3.5
4	[bmim][Cl]	1-butyl-3-methylimidazolium chloride	3.5	3.5
5	[bmim][DCA]	1-butyl-3-methylimidazolium dicyanamide	3.5	3.5
6	[bmim][(C2F5)3PF3]	1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate	3.5	3.5

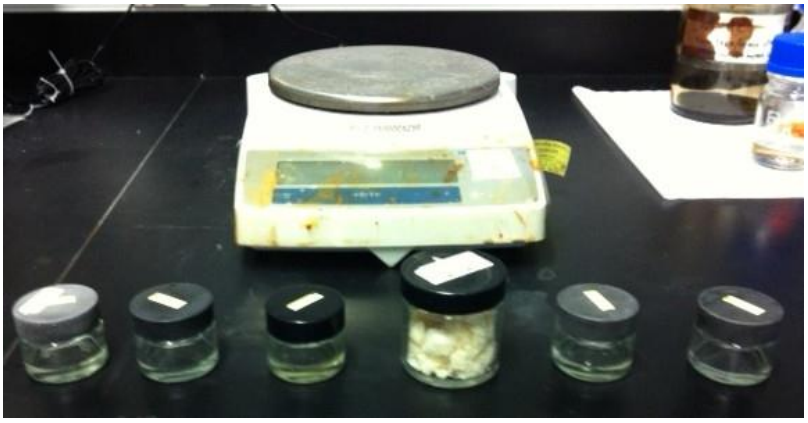
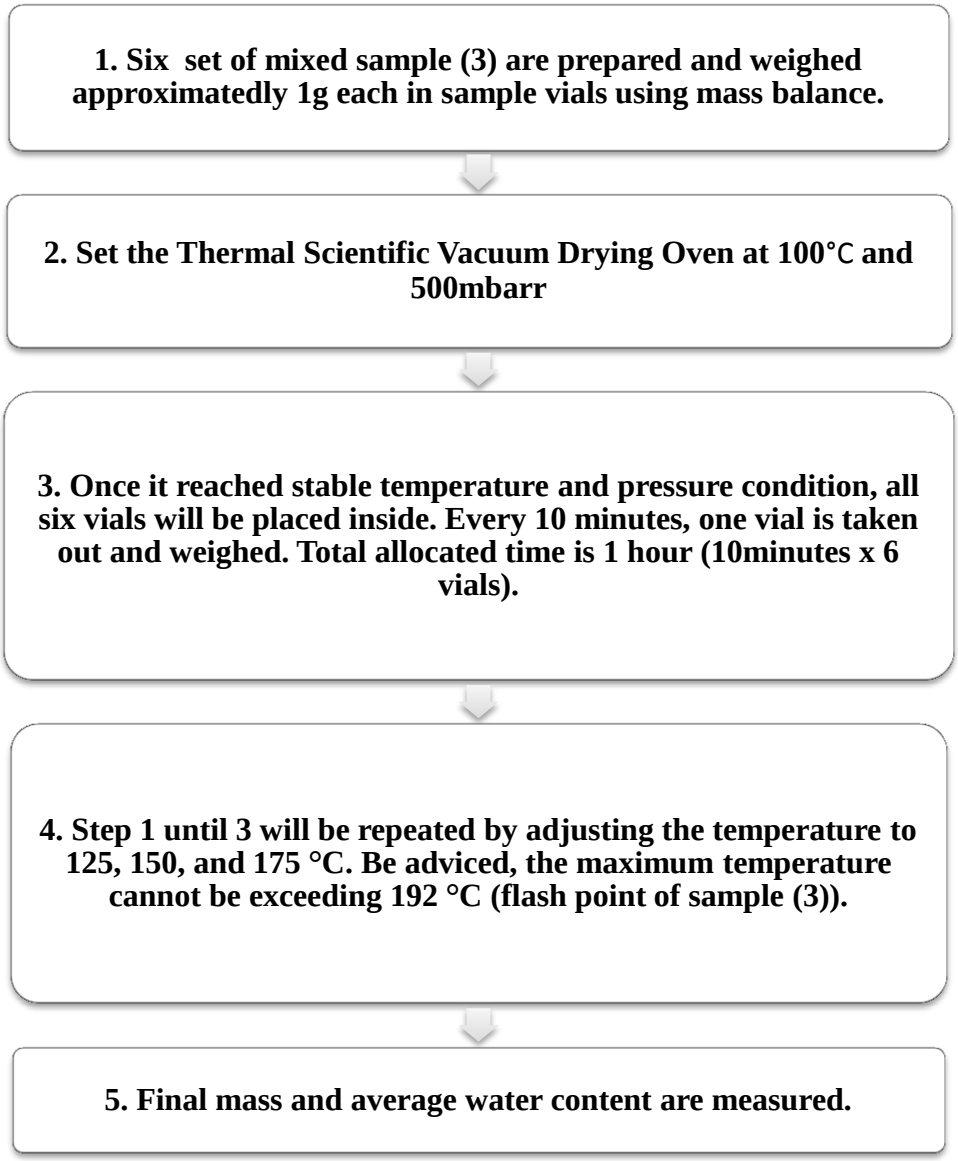


FIGURE 3.3 Sample Preparation;from left (1), (2), (3), (4), (5), and (6).

3.2 Research Methodology and Experimental Procedure/Approach

1. To investigate the effects of different operating temperature towards drying of ionic liquid

With the aim to check the effect of different operating temperature toward drying of ionic liquid, the main parameters are the operating temperature during and the drying rate of ionic liquids.



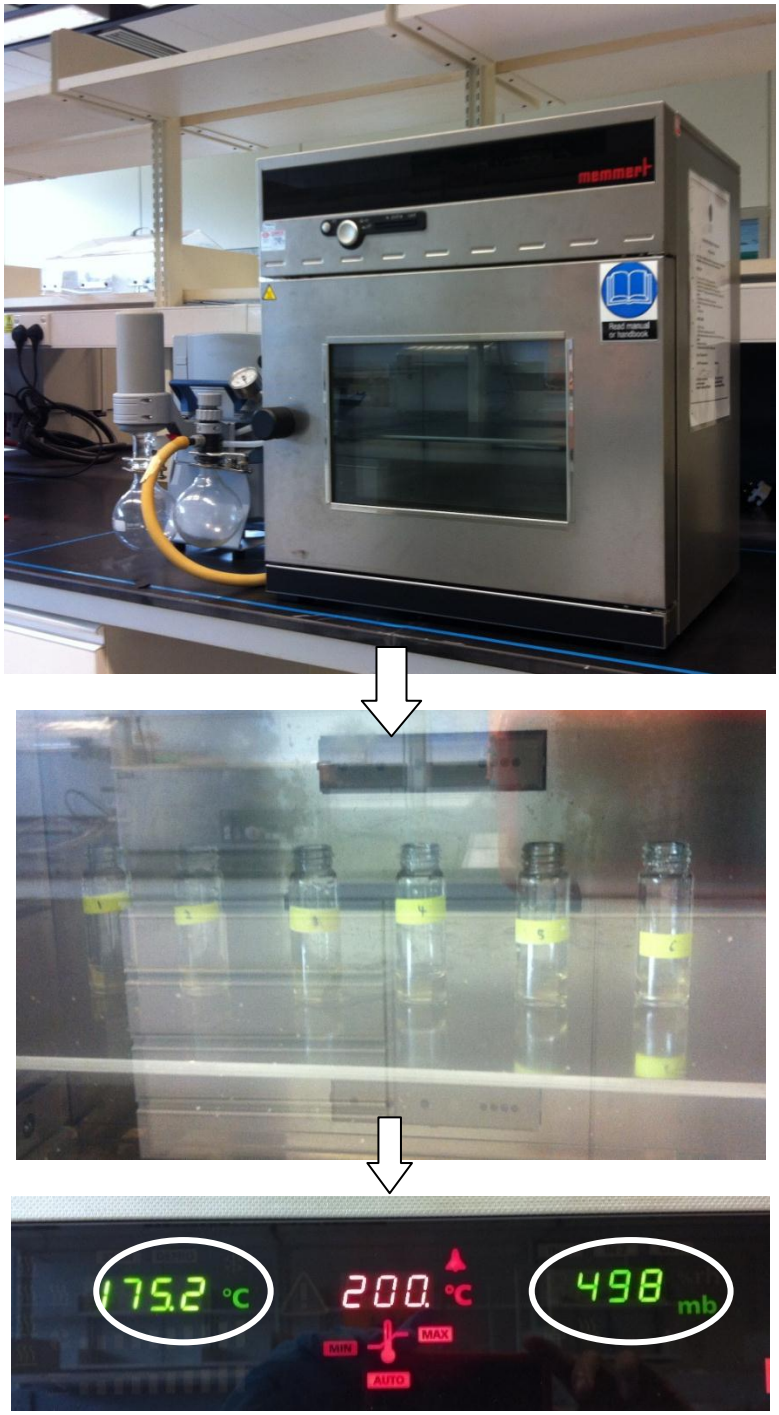
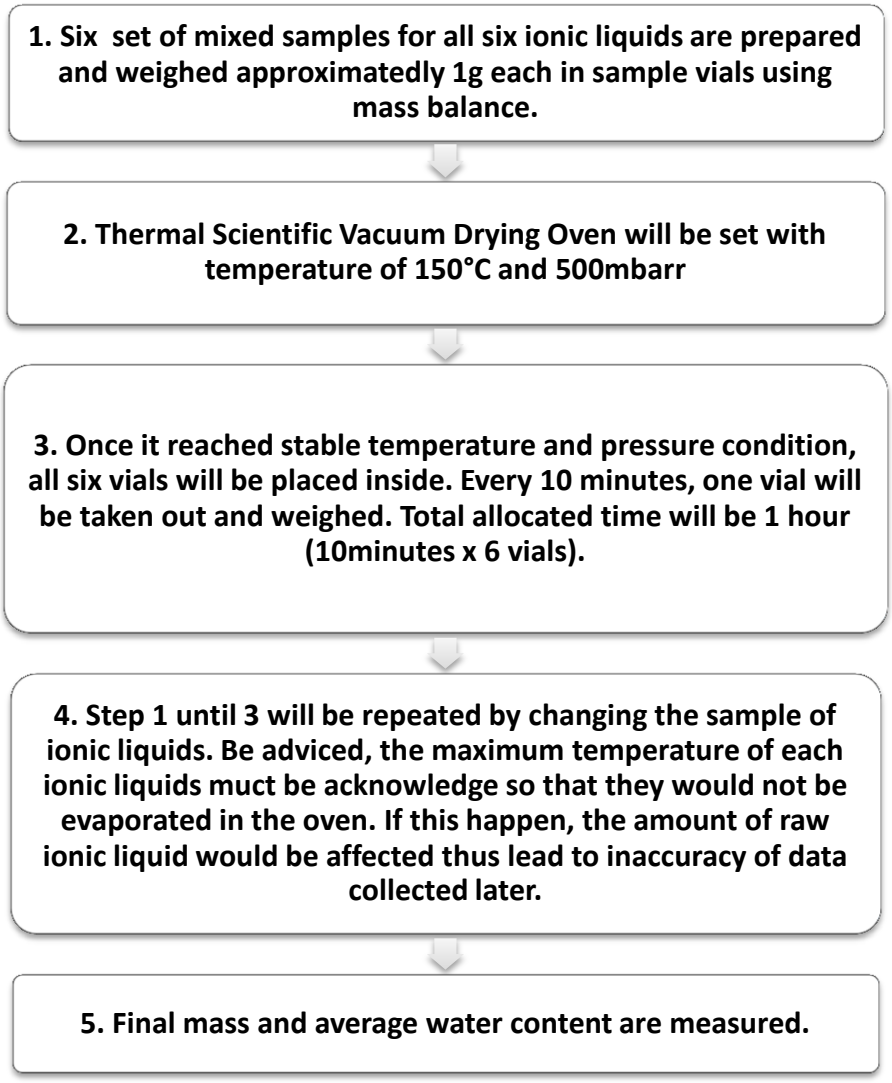


FIGURE 3.4 Sample Setup in Thermal Scientific Vacuum Drying Oven. Six sample vials are put inside and the cap must be opened. Acknowledge the temperature and pressure reading.

2. To investigate the effect of different anion and cation

The objective of this study is to investigate the effects of types of cation and anion of ionic liquids onto the drying behavior. The type of anion and cation can be decided based on size of ionic liquids as well as the ionic strength.



To investigate the effects of different cation in ionic liquids, the following samples will be used (consisted of sulfate and phosphate group):

- 1-butyl-3-methylimidazolium methylsulfate, [bmim][MeSO4]
- 1-ethyl-3-methylimidazolium hydrogensulfate, [emim][HSO4]
- 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate,[bmim][(C2F5)3PF3]
- 1,3-dimethylimidazolium dimethylphosphate, [mmim][DMP]

As for the anion part, we will use four different bmim-cation-based ionic liquids (bmim group):

- 1-butyl-3-methylimidazolium chloride, [bmim][Cl]
- 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]
- 1-butyl-3-methylimidazolium methylsulfate, [bmim][$MeSO_4$]
- 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [bmim][$(C_2F_5)_3PF_3$]

3. <u>To investigate the drying process of ionic liquid via different drying methods</u>

The heating temperature of Vacuum Drying Oven is set to 150°C at 500mbarr. After a stable temperature is achieved, solution of ionic liquid samples are placed in sample trays and left inside the oven before the vacuum pump is started. At 10 minutes interval, the vacuum pump is stopped and one ionic liquid sample is removed to weigh its current mass until a steady mass reading is achieved. The result of overall mass change over the period of 1 hour and final mass of samples are tabulated to generate drying curves for this method.

The initial water content of raw 1-butyl-3-methylimidazolium chloride is measured using Karl-Fischer titrator. Six samples of 0.5 g 1-butyl-3-methylimidazolium chloride mixed with 0.5 g distilled water (ionic liquid to water ratio of 1:1) are prepared and their initial mass is weighed in a sample vial using mass balance to ensure uniform mass for all samples.

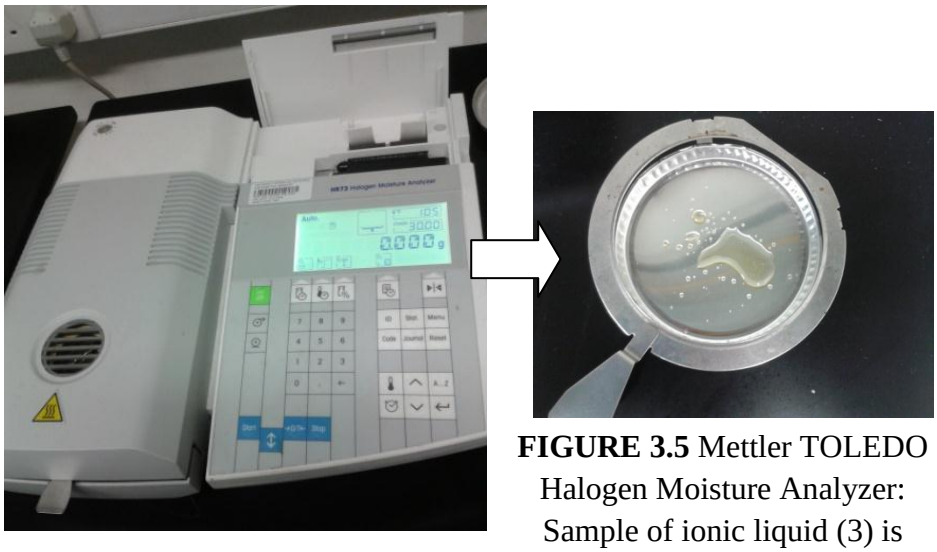


FIGURE 3.5 Mettler TOLEDO Halogen Moisture Analyzer: Sample of ionic liquid (3) is ready for analysis.

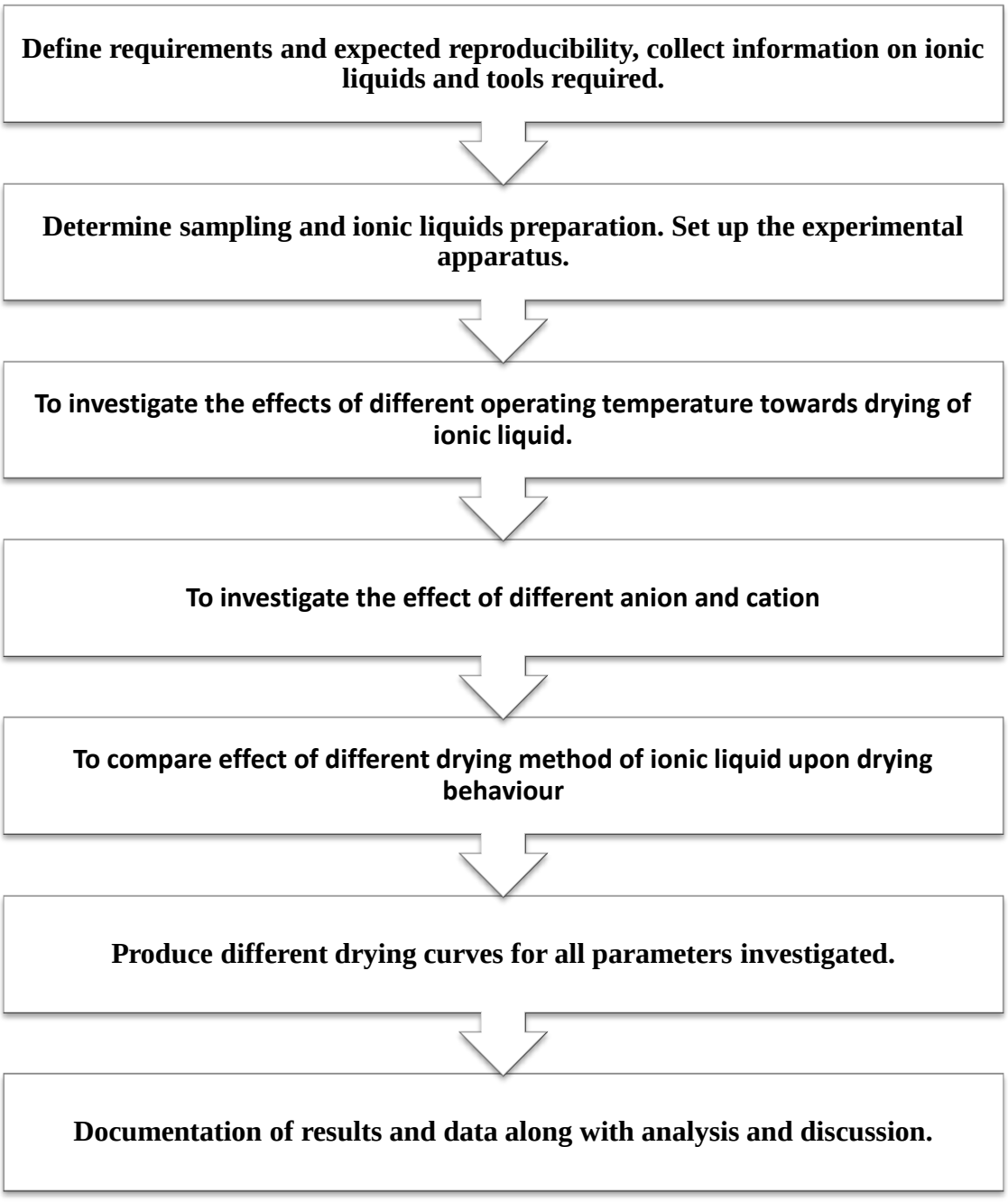
3.3 Chemicals, Equipment and Apparatus Required

TABLE 3.2 Equipment, Apparatus, and Chemical Used

Equipment	Therm Scientific Vacuum Drying Oven	Drying of ionic liquids measurement alternative 1
	METTLER TOLEDO Halogen Moisture Analyzer	Drying of ionic liquid measurement alternative 2
	METTLER TOLEDO Karl Fisher Titrator	Initial moisture content of raw ionic liquid measurement
	Mass Balance	Initial, intermediate, and final mass reading of sample primary measurement
	Differential Scanning Calorimetry	Initial, intermediate, and final mass reading of sample secondary measurement
Apparatus	Sample Vials	Ionic liquid sample placement
	Spatula	Raw ionic liquid sample preparation
	Parafilm	Containment of ionic liquid sample
	Labeling Stickers	Sample Vials labeling
Chemical	Ionics Liquids	1. 1-butyl-3-methylimidazolium methylsulfate 2. 1-ethyl-3-methylimidazolium hydrogensulfate 3. 1,3-dimethylimidazolium dimethylphosphate 4. 1-butyl-3-methylimidazolium chloride 5. 1-butyl-3-methylimidazolium dicyanamide 6. 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate

3.4 Key Milestones

Several key milestones for this research project must be achieved in order to meet the objective of this project:



3.5 Gantt Chart.

The gantt chart can be categorized into two phase; first phase is as what has been prepared by the student him/herself in conjunction with their project timeline suited with supervision of respective lecturer which aim more toward theoretical value and strengthening basic knowledge on the topic itself before starting experimental procedure during FYP I. This followed by the second phase which focusing more towards experimental processes by manipulating the objectives prepared from FYP II to be done during FYP II.

No	Detail/Week (FYP I)	1	2	3	4	5	6	7		9	10	11	12	13	14
1	Research Work for Ionic Liquids and Drying Process (theory)								Midsem Break						
2	Preparation of Ionic Liquid samples and equipment (experiment)														
3	Setting of parameters and Operating Condition														
4	Initial testing for experimental setup and data gathering														
5	Adjustment/reset objectives, procedure, and literature review														
6	Weekly Meeting with supervisor														
No	Detail/Week (FYP II)	1	2	3	4	5	6	7		9	10	11	12	13	14
1	Determine the effect of temperature on drying of Ionic Liquid								MidSem Break						
2	Determine the effect cation/anion on drying of Ionic Liquid														
3	Determine the effect of drying methods on drying of Ionic Liquid														
4	Data gathering, synthesis and analysis of drying curves for each parameter														
5	Interpretation of drying curves for each parameter														
6	Compilation of data analysis and Conclusion														

CHAPTER 4

RESULT AND DISCUSSION

This chapter presents the finding and outcome of the project work done on kinetic of drying for ionic liquid. All the gathered data from the project work are presented in the form of tables and figures including graphs showing drying curves for all the objectives studied. The data had been analyzed and results had been discussed accordingly with regard to drying of ionic liquid and its kinetic data.

4.1 Overview

For the experiments described above, the raw data will be the total moisture evaporated from the Thermal Scientific Vacuum Drying Oven for a period of 60 minutes in 10 minutes interval for every reading. A period of 60 minutes is chosen due to the indication from initial samples testing whereby equilibrium moisture content for most ionic liquid samples are achieved in that duration. By taking into consideration the boiling point of water, the temperature is set at 150°C in order to dry the water content in the samples.

Thermogravimetric analysis (TGA), which can follow weight loss over a wide temperature range or over a long period of time at a specific temperature, on small (10-100 mg) samples, is a technique which rapidly provides data for understanding drying processes. The results yield not only quantitative information about the amount of moisture present, but also information about the rate of weight loss which can be used to determine kinetic parameters according to drying curves obtained.

4.2 Effect of Drying Temperature

The data obtained from the experiments are indicated in APPENDIX below showing the change in moisture content and drying rate over time for temperature settings of 100°C, 125°C, 150°C, and 175°C with constant ratio of ionic liquid to initial water content (ratio of 1:1).

The ionic liquid used is sample (3) for all setup. The moisture content is extracted directly from the mass balance reading in percentage from 100% to equilibrium moisture content. Whereby the drying rate is calculated based on the initial and current weight of ionic liquid sample over a period of time using the formula below:

$$Drying\ rate\ (g/min) = \frac{Initial\ weight(g) - Current\ weight(g)}{time(\text{min})}$$

4.2.1 Drying Curves

From the results obtained, Figure 4.1 resembles exactly that of typical moisture content plot for normal drying process whereby the graphs decrease at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content of the sample under the desired temperature. This is possible since the ionic liquid samples are prepared such that it is initially saturated with water content and thus, with sufficient heating under suitable temperature, the water content is gradually released to dry the ionic liquid. However, the final moisture content of the dried ionic liquid sample is not exactly 0%. There is still some percentage of moisture content available since it is well known that water is omnipresent in ionic liquids. Dry ionic liquid will absorb water from atmosphere especially when heat is applied to it. Imidazolium based ionic liquids in particular are extremely hygroscopic and they absorb water from atmosphere. These are the reasons why the ionic liquid samples need to be initially saturated with water and the final moisture content after drying is only between 40% and 50%.

For drying of all samples, the experiments are repeated twice to ensure data accuracy and repeatability. Error bars based on standard deviations between the first and second trials are presented in Figure 4.1. Since it is observable that the error bars are very small due to very low value of standard deviations, they can be assumed as negligible for all samples. The values of standard deviation for all samples are tabulated in APPENDIX.

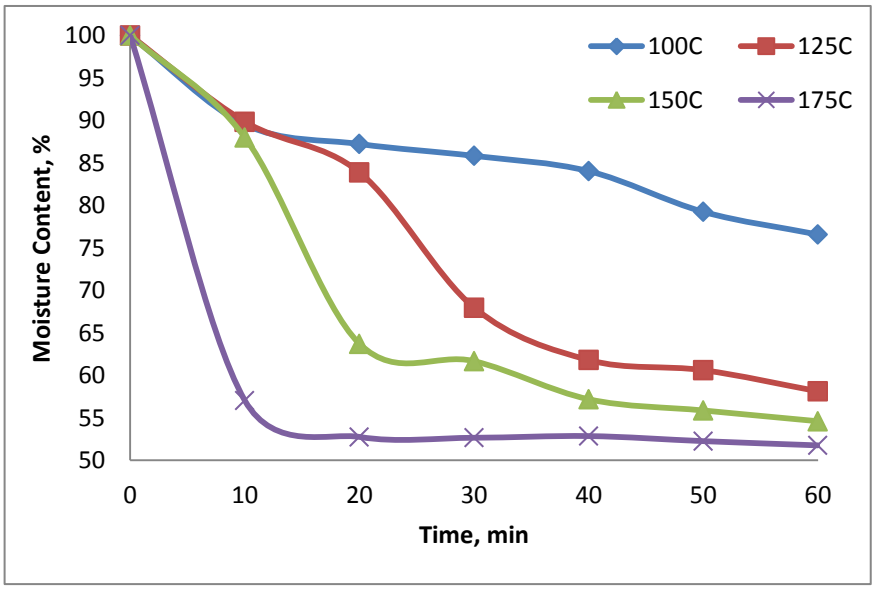


FIGURE 4.1 Drying Curve of Moisture Content versus Time at Different Temperatures (using ionic liquid sample (3))

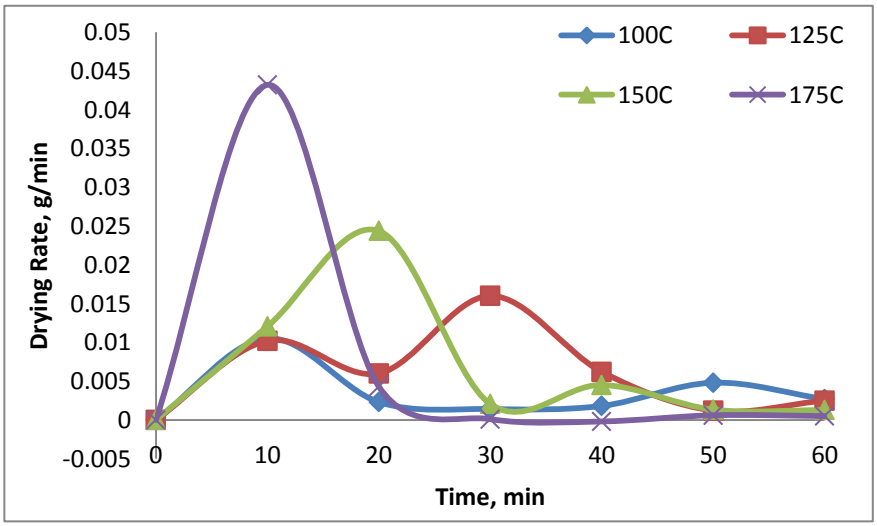


FIGURE 4.2 Drying Curve of Drying Rate versus Time at Different Temperatures (using ionic liquid sample (3))

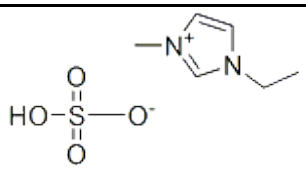
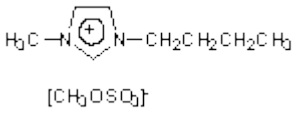
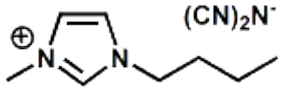
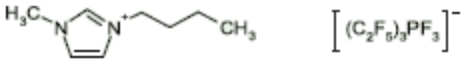
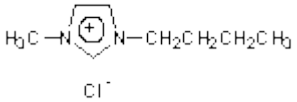
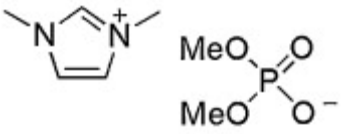
Referring to Figure 4.2, the shape of the drying rate curve is different to the typical drying rate curve shown in Chapter 2. There are only two phases of drying, initial period and falling rate period observed from the plots. Each operating temperature indicate different highest drying rate. It is highest at the first 10 minutes of continuous drying for operating temperature of 175°C, first 20 minutes for 150°C, followed by the highest of 125°C ten minutes after and lastly 100°C 10 minutes after. This is the result of low internal resistance of moisture at the beginning of drying. Therefore, when energy is impacted, moisture can easily move to surface to be evaporated. As the drying progressed, more energy is needed due to the hygroscopic characteristic of ionic liquid which hinders the migration of moisture from the inner interstices of each particle to the outer surface. Consequently, the drying rate decreases gradually in the falling rate period and becomes zero.

4.3 Effect of Different Types of Cation and Anion

The data obtained from the experiments are indicated in Figures 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8 showing the change in moisture content and drying rate over time for different types of ionic liquid with constant ionic liquid to initial water content ratio of 1:1 and drying temperature settings of 150°C. The ionic liquids used are:

i. 1-butyl-3-methylimidazolium chloride, [bmim][Cl]
ii. 1-butyl-3-methylimidazolium dicyanamide, [bmim][DCA]
iii. 1-butyl-3-methylimidazolium methylsulfate, [bmim][$MeSO_4$]
iv. 1-ethyl-3-methylimidazolium hydrogensulfate, [emim][HSO_4]
v. 1-butyl-3-methylimidazolium tris(pentafluoroethyl)-trifluorophosphate, [bmim][$(C_2F_5)_3PF_3$]
vi. 1,3-dimethylimidazolium dimethylphosphate, [mmim][DMP]

TABLE 4.1 Molecular Structures of Ionic Liquid

Ionic Liquid	Molecular Structure
[emim][HSO_4]	
[bmim][$MeSO_4$]	
[bmim][DCA]	
[bmim][$(C_2F_5)_3PF_3$]	
[bmim][Cl]	
[mmim][DMP]	

The different samples of ionic liquids are chosen based on their alkyl chain and size of anion. Different length of alkyl chain comprising of butyl, ethyl and dimethyl may affect many ionic liquid properties especially its size and density resulting in different abilities in holding and dissociating water molecules between ionic liquid particles. In addition, it is also desired to observe the behaviour of drying curve for different ionic liquid anion (SO_4 and phosphate) to see the extent of hydrogen bonding between the anion and water molecules inside the ionic liquid and the effect on its drying kinetic. To compare the effects of different types of cation and anion towards drying curve of these ionic liquid samples, the plots are separated into three categories based on similar cation or anion:

i. [bmim] cation (Figure 4.3 and 4.4)
ii. [SO_4]- anion (Figure 4.5 and 4.6)
iii. Phosphate-containing anion (Figure 4.7 and 4.8)

4.3.1 Drying Curves

From all the results obtained, the plot of moisture content is similar to that of typical moisture content plot for normal drying process whereby the graphs initially decrease at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content. The reason behind this is as explained in previous section for the Effect of Drying Temperature. Referring to the drying rate curve of all types of ionic liquid samples, the shape of the curve is different to the typical drying rate curve shown in Chapter 2. There are only two phases of drying, initial period and falling rate period observed from the plots similar to the previous results of different drying temperatures and initial water contents.

In addition, from Figure 4.3, the shapes of the graph are very similar to each other with final moisture content ranging around 45% for all four samples which shows the role of [bmim] cation in determining the extent to which water molecules can be stored and subsequently released in the ionic liquid samples. However, the moisture content decreases fastest with highest maximum drying rate and in largest amount for [bmim][$MeSO_4$] and the lowest amount of dehydration with minimum drying rate is observed for [bmim][$(C_2F_5)_3PF_3$] due to the different extent of hydrogen bonding between the water molecules and the anion in the four samples. When paired with the 1-butyl-3-methylimidazolium cation, the hydrogen-bond basicity of the anion determines the amount of energy needed to break the water molecules bond from ionic liquid particles and consequently this will also affect its kinetic of drying.

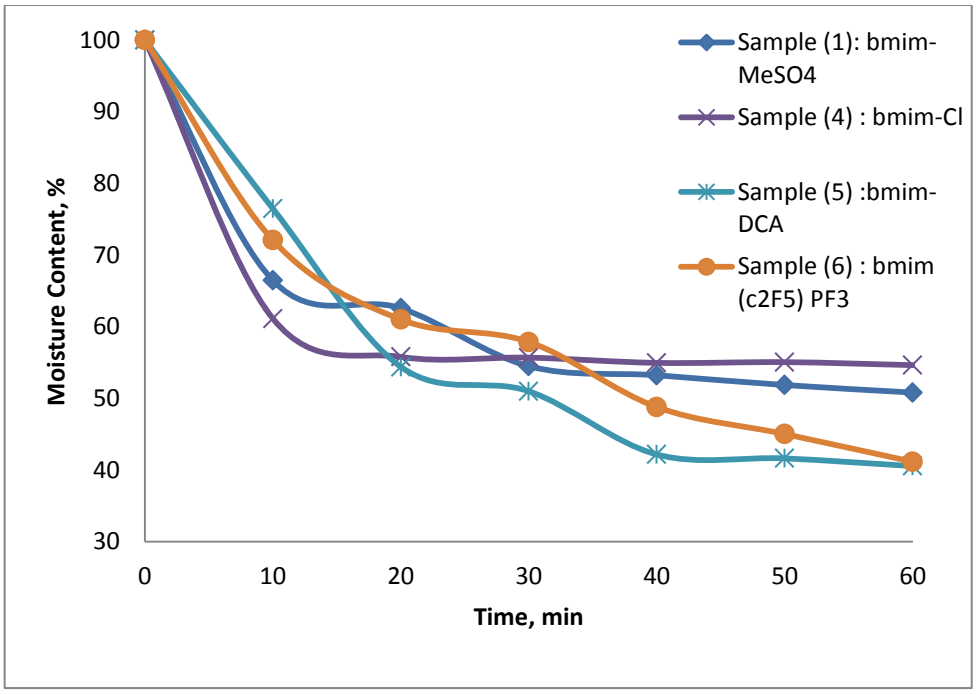


FIGURE 4.3 Drying Curve of Moisture Content versus Time for [bmim] Cation

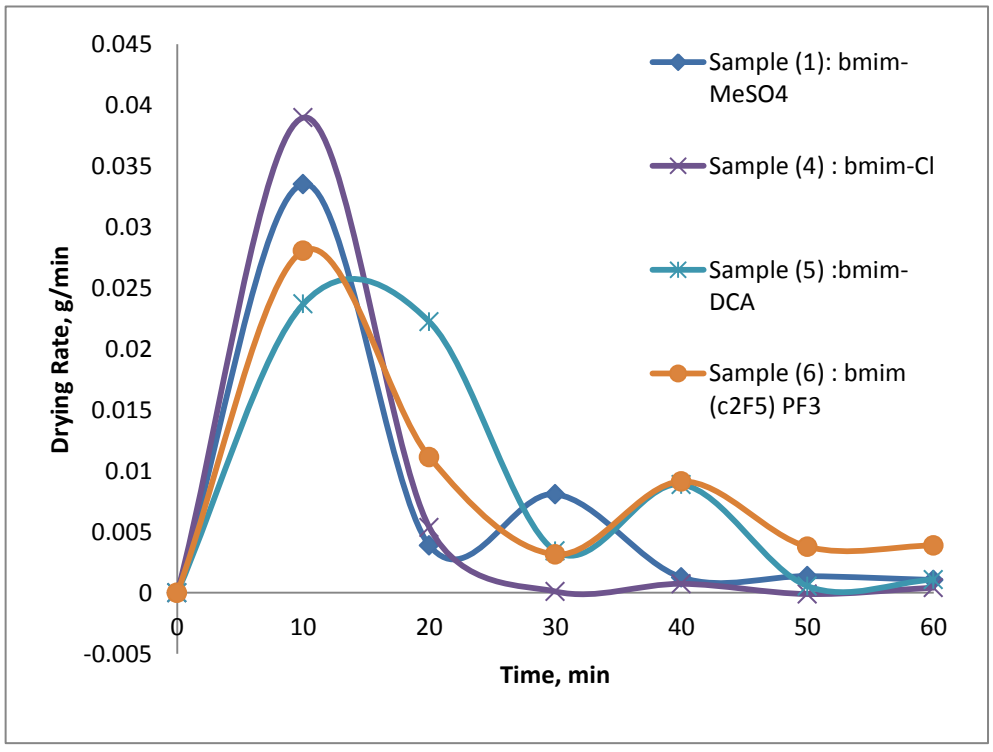


FIGURE 4.4 Drying Curve of Drying Rate versus Time for [bmim] Cation

Moving on to Figure 4.5 and 4.6, the shapes of the graph are very similar to each other. However, the moisture content decreases slower with higher minimum drying rate and in smaller amount for [emim][HSO_4] compared to [bmim][$MeSO_4$] with final moisture content of 53.52% for [emim][HSO_4] and 50.82% for [bmim][$MeSO_4$]. This is due to the different length of alkyl chain whereby [emim][HSO_4] chain is shorter than [bmim][$MeSO_4$]. Longer alkyl chain has more free volume which enables more water molecules to be contained and bonded with the ionic liquid particles resulting in slower drying process. [emim][HSO_4] also shows the closest resemblance to the typical drying rate curve with all three phases of drying including the constant rate period. Furthermore, during the experiment, the sample of [emim][HSO_4] tends to vaporize especially when heat is applied to it resulting in greater reduction in its weight after drying. It is also observed that the drying process stops after 20 minutes for [emim][HSO_4] which is faster than [bmim][$MeSO_4$].

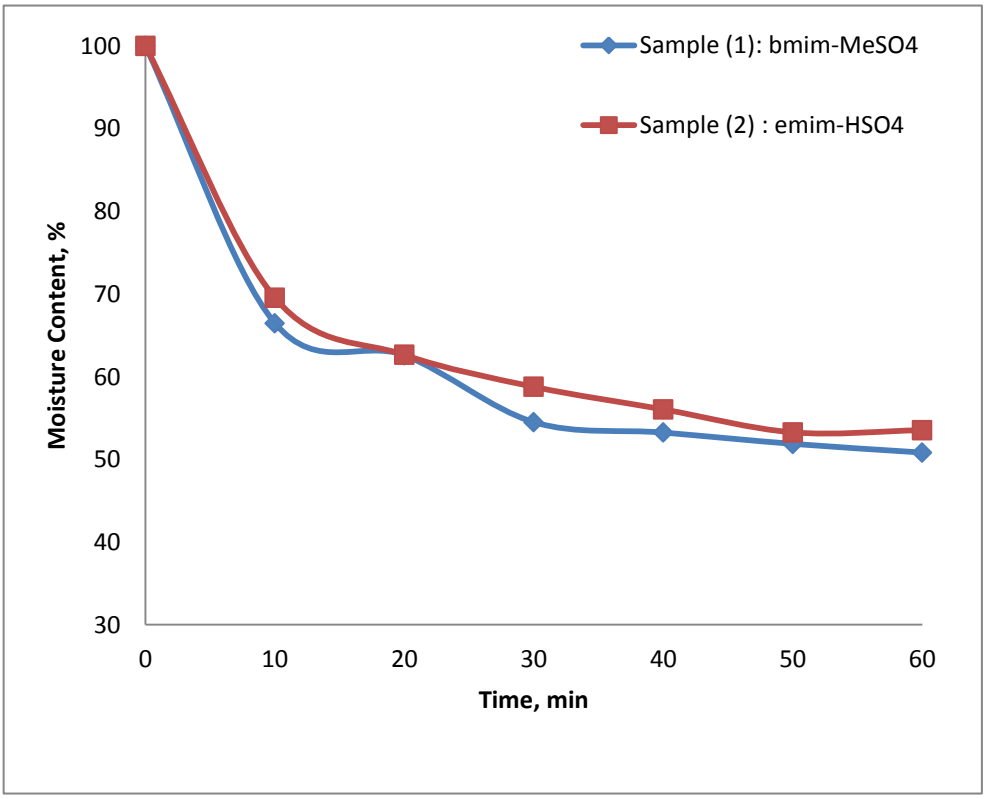


FIGURE 4.5 Drying Curve of Moisture Content versus Time for [SO_4]- Anion

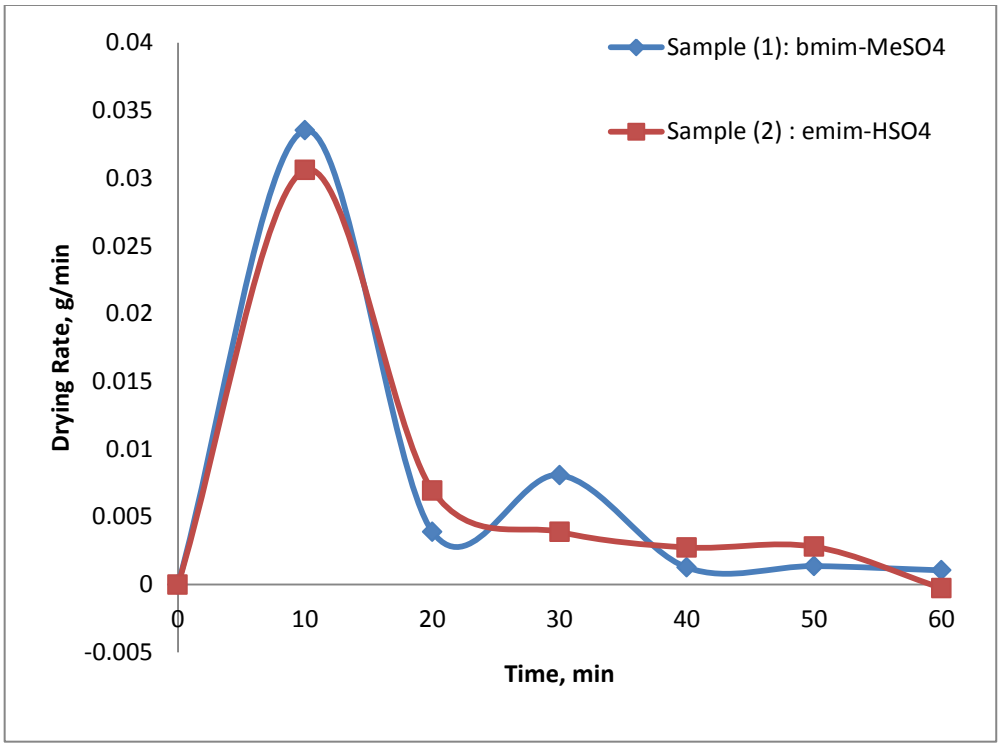


FIGURE 4.6 Drying Curve of Drying Rate versus Time for $[SO_4]$- Anion

Finally, referring to Figure 4.7 and 4.8, the shapes of the graph are very similar to each other with final moisture content of 41.16% for [bmim][$(C_2F_5)_3PF_3$] and 53.6% for [mmim][DMP]. Although the alkyl chain of [mmim][DMP] is shorter, it contains more water after the drying process due to the stronger hydrogen bonding between its anion and water molecules compared to [bmim][$(C_2F_5)_3PF_3$].

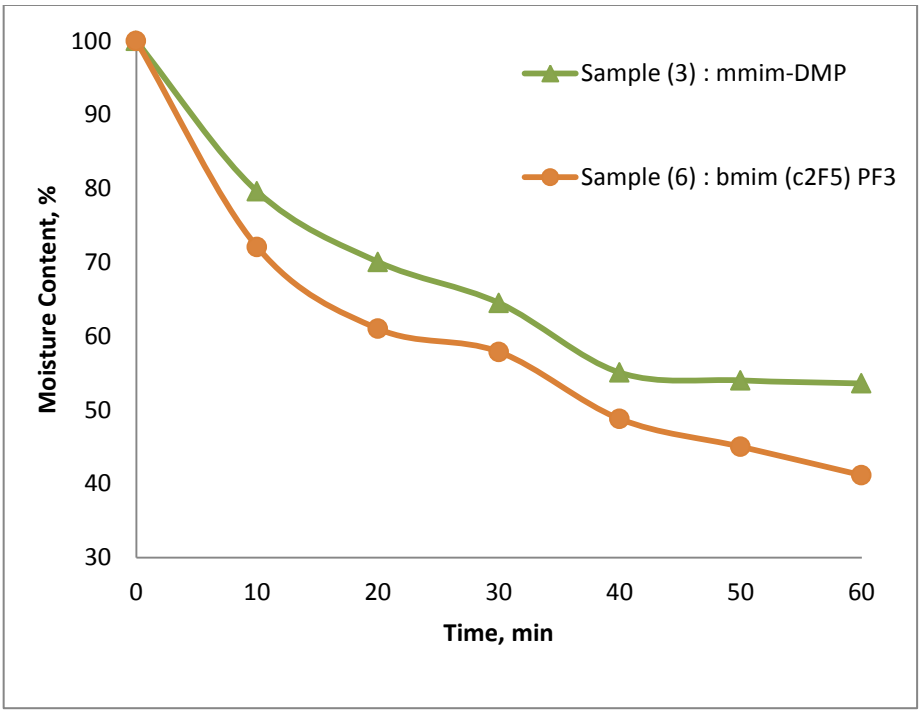


FIGURE 4.7 Drying Curve of Moisture Content versus Time for Phosphate Anion

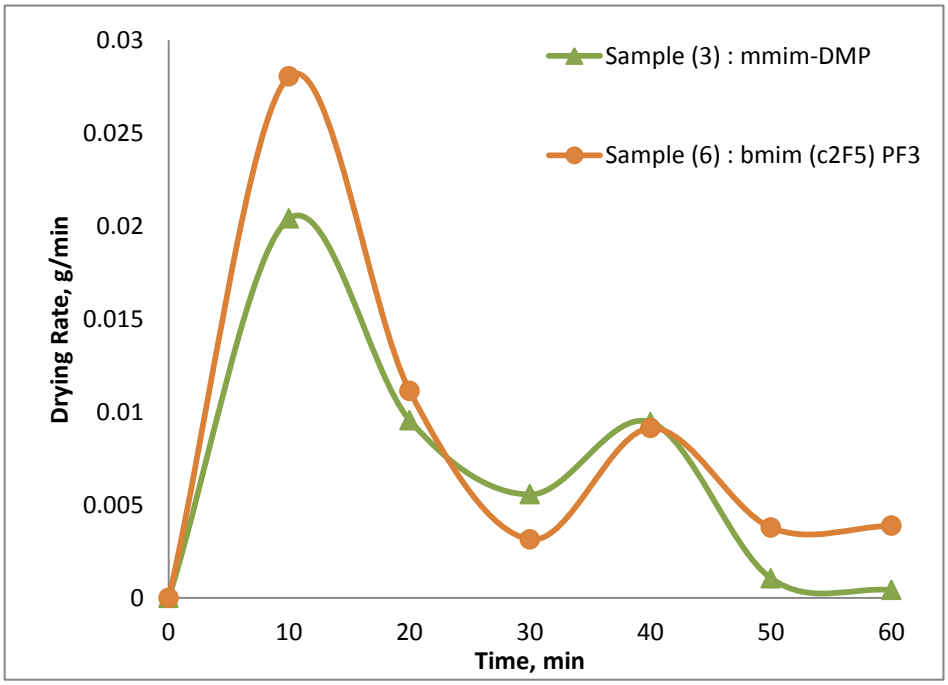


Figure 4.8 Drying Curve of Drying Rate versus Time for Phosphate Anion

4.4 Effect of Different Drying Methods

The data obtained from the experiments are indicated in Figures 4.9 and 4.10 showing the change in moisture content and drying rate over time for drying of 1-butyl-3-methylimidazolium chloride using vacuum drying compared with halogen lamp drying with constant drying temperature settings of 150°C and ionic liquid to water ratio of 1:1. The reason for choosing vacuum drying oven as an primary method to dry ionic liquid samples is due to this method is a conventional and widely used method for drying laboratory samples since it is economical and less complex. In recent years, vacuum drying technology is also combined with microwave heating technology and other drying technologies. The results obtained from the Halogen Moisture Analyzer will be compared with drying curves generated from vacuum drying method mentioned earlier to analyze its efficiency and performance in drying process of ionic liquid samples.

4.4.1 Drying Curves

For vacuum drying method, the plot of moisture content is similar to that of typical moisture content plot for normal drying process whereby the graph initially decreases at higher slopes and gradually coming into a constant moisture content which is indicated by the equilibrium moisture content. Referring to the drying rate curve, the shape of the curve using vacuum drying oven is different to the typical drying rate curve. There are only two phases of drying, initial period and falling rate period, whereby moisture transfer within ionic liquid particles is dominated by internal diffusion.

In addition, comparing the drying curves between vacuum drying and Halogen Moisture Analyzer at 150°C, the shapes of the graph are quite different from each other with lower final moisture content achieved for halogen moisture analyzer method. Furthermore, the moisture content decreases fastest and in largest amount in halogen moisture analyzer since the maximum drying rate is higher than vacuum oven.

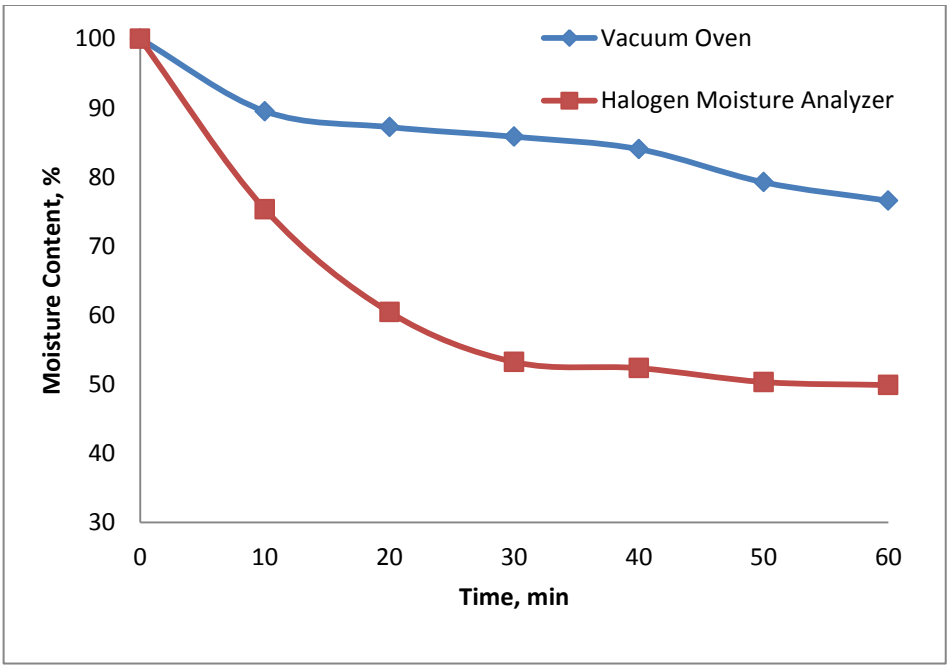


FIGURE 4.9 Comparison of Drying Curves for Moisture Content versus Time

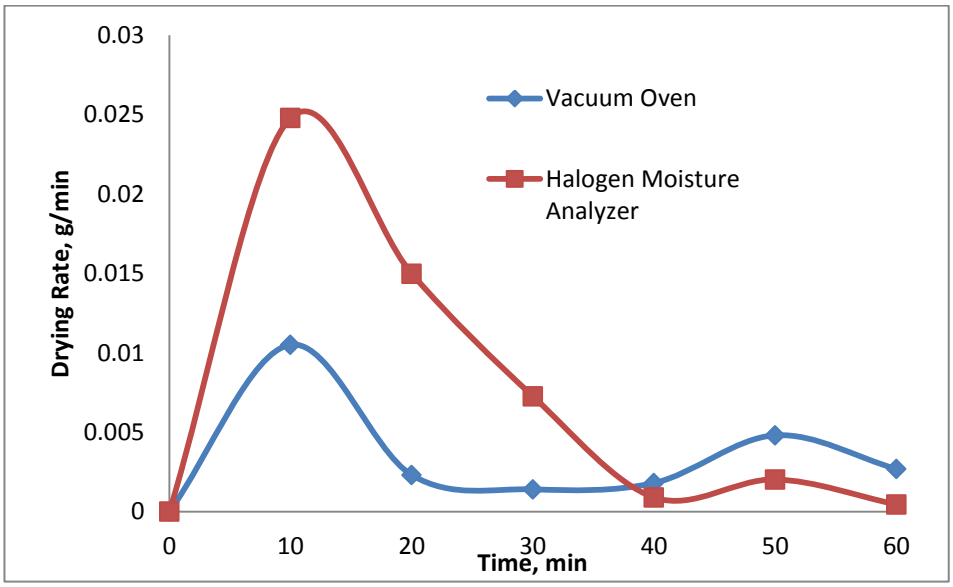


FIGURE 4.10 Comparison of Drying Curves for Drying Rate versus Time

CHAPTER 5

CONCLUSION AND RECOMMENDATION

In conclusion, the drying curves and kinetic of drying under each objectives outlined before which are drying temperatures, different combination of cation and anion, and also alternative drying methods have been analyzed in this paper. The effects of all those parameters are presented in the form of drying curves showing the change in moisture content percentage and drying rate over time are done to obtain their drying rate constant and drying time.

For the study on the effects of three different parameters on drying curves of ionic liquid, the following conclusion can be made. There are only two phases of drying in the drying rate curve of ionic liquid which are initial or rising rate period and falling rate period.

From the primary drying curves, manipulation of data which lead to secondary data for kinetic analysis can be made for all the different parameters with the following conclusion:

i. The higher the drying temperature, the higher the drying constant with shorter drying time achieved.
ii. The higher the initial ratio of ionic liquid to water in sample solution, the higher the drying constant with shorter drying time achieved.
iii. The smaller the molecular size of ionic liquid anion, the higher the drying constant with shorter drying time achieved with fastest drying observed for samples containing $[SO_4]$- anion.
iv. Halogen Moisture Analyzer method has higher drying constant with shorter drying time which shows faster speed of drying compared to Vacuum Drying Oven.

Furthermore, the study on drying of ionic liquid is feasible in terms of its scopes and objectives whereby they are achievable and relevant to the scientific society.

Nevertheless, there are recommendations that can be made in order to expand the scope of study for future uses.

i. To investigate effect of anion and cation of ionic liquid with different hydrocarbon chain, structures, and bonding strength.
ii. To investigate the effect of the existence of solid support (activated carbon) onto the drying behavior of the ionic liquid.
iii. To repeat each objectives minimum five times for accuracy and precision of the data collected.

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APPENDIX

EXPERIMENTAL DATA

1. Data for Different Ionic Liquid Experiment

Sample (1): bmim-MeSO4

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	0.979	1.021	1	0.029698	0
10	66.465	0.6963	0.633	0.66465	0.04476	0.033535
20	62.58	0.6556	0.596	0.6258	0.042144	0.003885
30	54.495	0.5709	0.519	0.54495	0.036699	0.008085
40	53.235	0.5577	0.507	0.53235	0.03585	0.00126
50	51.87	0.5434	0.494	0.5187	0.034931	0.001365
60	50.82	0.5324	0.484	0.5082	0.034224	0.00105

Sample (2) : emim-HSO4

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	1.003	1.007	1.005	0.002828	0
10	69.5403	0.73216	0.6656	0.69888	0.047065	0.030612
20	62.63433	0.65945	0.5995	0.629475	0.042391	0.00694
30	58.76866	0.61875	0.5625	0.590625	0.039775	0.003885
40	56.04179	0.59004	0.5364	0.56322	0.037929	0.002741
50	53.26269	0.56078	0.5098	0.53529	0.036048	0.002793
60	53.52388	0.56353	0.5123	0.537915	0.036225	0.00026

Sample (3) : mmim-DMP

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	0.998	1.004	1.001	0.004243	0
10	79.61538	0.8349	0.759	0.79695	0.053669	0.020405
20	70.06993	0.7348	0.668	0.7014	0.047235	0.009555
30	64.51049	0.6765	0.615	0.64575	0.043487	0.005565
40	55.06993	0.5775	0.525	0.55125	0.037123	0.00945
50	54.02098	0.5665	0.515	0.54075	0.036416	0.00105
60	53.6014	0.5621	0.511	0.53655	0.036133	0.00042

Sample (4) : bmim-Cl

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	1	1.006	1.003	0.004243	0
10	61.13659	0.6424	0.584	0.6132	0.041295	0.03898
20	55.79761	0.5863	0.533	0.55965	0.037689	0.005355
30	55.69292	0.5852	0.532	0.5586	0.037618	0.000105
40	54.96012	0.5775	0.525	0.55125	0.037123	0.000735
50	55.06481	0.5786	0.526	0.5523	0.037194	0.00011
60	54.64606	0.5742	0.522	0.5481	0.036911	0.00042

Sample (5) :bmim-DCA

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	1.004	1.01	1.007	0.004243	0
10	76.4717	0.80674	0.7334	0.77007	0.051859	0.023693
20	54.39772	0.57387	0.5217	0.547785	0.03689	0.022229
30	50.99851	0.53801	0.4891	0.513555	0.034585	0.003423
40	42.17726	0.44495	0.4045	0.424725	0.028602	0.008883
50	41.63505	0.43923	0.3993	0.419265	0.028235	0.000546
60	40.56107	0.4279	0.389	0.40845	0.027506	0.001082

Sample (6) : bmim (c2F5) PF3

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	1.001	1.009	1.005	0.005657	0
10	72.08955	0.759	0.69	0.7245	0.04879	0.02805
20	61.01493	0.6424	0.584	0.6132	0.041295	0.01113
30	57.8806	0.6094	0.554	0.5817	0.039174	0.00315
40	48.79104	0.5137	0.467	0.49035	0.033022	0.009135
50	45.02985	0.4741	0.431	0.45255	0.030476	0.00378
60	41.16418	0.4334	0.394	0.4137	0.02786	0.003885

2. Data for Different Operating Temperature Experiment

100°C

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	1	1.004	1.002	0.002828	0
10	89.52096	0.888	0.906	0.897	0.012728	0.0105
20	87.22555	0.857	0.891	0.874	0.024042	0.0023
30	85.82834	0.862	0.858	0.86	0.002828	0.0014
40	84.03194	0.853	0.831	0.842	0.015556	0.0018
50	79.24152	0.779	0.809	0.794	0.021213	0.0048
60	76.56687	0.7769	0.7575	0.7672	0.013718	0.00268

125°C

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	1	1.01	1.005	0.007071	0
10	89.85075	0.889	0.917	0.903	0.019799	0.0102
20	83.8806	0.872	0.814	0.843	0.041012	0.006
30	67.9602	0.69	0.676	0.683	0.009899	0.016
40	61.79104	0.61	0.632	0.621	0.015556	0.0062
50	60.59701	0.605	0.613	0.609	0.005657	0.0012
60	58.10945	0.57	0.598	0.584	0.019799	0.0025

150°C

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	0.994	1.012	1.003	0.012728	0
10	87.999	0.92466	0.8406	0.88263	0.059439	0.012037
20	63.7014	0.66935	0.6085	0.638925	0.043027	0.024371
30	61.66002	0.6479	0.589	0.61845	0.041649	0.002048
40	57.16899	0.60071	0.5461	0.573405	0.038615	0.004504
50	55.84995	0.58685	0.5335	0.560175	0.037724	0.001323
60	54.58325	0.57354	0.5214	0.54747	0.036869	0.001271

175°C

Time (min)	Moisture Content%	Average	1st trial (g)	2nd Trial (g)	Standard Deviation	Drying rate (g/min)
0	100	0.99	1.02	1.005	0.021213	0
10	57.01493	0.562	0.584	0.573	0.015556	0.0432
20	52.73632	0.527	0.533	0.53	0.004243	0.0043
30	52.63682	0.526	0.532	0.529	0.004243	0.0001
40	52.83582	0.537	0.525	0.531	0.008485	0.0002
50	52.23881	0.524	0.526	0.525	0.001414	0.0006
60	51.74129	0.518	0.522	0.52	0.002828	0.0005